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Deep-Level Emission Tailoring in ZnO Nanostructures Grown via Hydrothermal Synthesis

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Abstract. Development of the new approaches for synthesis of luminescent semiconductor nanomaterials is of high demand. In this work, nano- and microstructures of zinc oxide were synthesized by the hydrothermal method to provide new insight onto the optimization of this material optical properties. The possibility of controlling the synthesized ZnO geometry and morphology using various surfactants during the synthesis was demonstrated. Further study of the structures obtained by PL spectroscopy made it possible to observe a correlation between the hydrothermal growth conditions and the obtained ZnO nanostructures optical properties. This property, together with the ability to control the structures geometry, opens up new possibilities for their application in nanophotonics, UV-VIS and white light sources.

Keywords: zinc oxide, hydrothermal, nanowire, photoluminescence, deep level emission, PEI, sodium citrate

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Глубокоуровневое излучение в наноструктурах ZnO, выращенных методом гидротермального синтеза

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Аннотация. Разработка новых подходов к синтезу люминесцентных полупроводниковых наноматериалов является в настоящее время актуальной задачей. В данной работе гидротермальным методом были синтезированы нано- и микроструктуры оксида цинка, что позволило по-новому взглянуть на оптимизацию оптических свойств этого материала. Показана возможность управления геометрией и морфологией синтезированного ZnO с помощью различных поверхностно-активных веществ, используемых в процессе синтеза. Дальнейшее изучение структур методом спектроскопии ФЛ позволило обнаружить корреляцию между гидротермальными условиями роста и оптическими свойствами полученных наноструктур ZnO. Это свойство вместе с возможностью управления геометрией структур открывает новые возможности для их применения в нанофотонике, источниках УФ-видимого и белого света.

Ключевые слова: оксид цинка, гидротермальный синтез, нитевидные нанoктристаллы, фотолюминесценция, глубокоуровневая эмиссия, полиэтиленимин, цитрат натрия

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Introduction

Nano- and micro-sized structures find a wide range of applications in various fields from sensors [1] to UV [2, 3] and visible range emitters [4]. One promising material for modern research is zinc oxide. Zinc oxide is a technologically feasible, abundant, chemically stable, and non-toxic wide-gap semiconductor material that was actively studied during the last decades. Wide bandgap (3.37 eV at room temperature (RT) in a bulk) and large exciton binding energy (60 meV), which is much higher than thermal energy at RT make it an excellent candidate for the development of UV light sources [5].

The promising method for the growth of ZnO nanostructures is hydrothermal synthesis [6, 7]. The advantages of this include vast control over the growth conditions, low synthesis temperatures (less than 100 °C) [6, 7], providing significant reduction in energy consumption and making this technique technologically feasible. Using the hydrothermal synthesis, it is possible to obtain nanostructures of various geometries and on various substrates, both lattice-matched and not, classical ones – silicon, sapphire and silicon carbide [8–10], transparent and even flexible [11, 12]. Despite the wide range of works on the hydrothermal synthesis, study and device application of ZnO nanostructures, there have been no systematic studies aimed at simultaneously controlling the geometry of such objects and studying the growth conditions effect on their optical properties. In this work, samples obtained by hydrothermal synthesis with addition of surfactants are thoroughly studied to demonstrate that change in the growth solution chemistry provides not only ability for control over the nanostructures morphology but also affects the luminescent properties of the structures allowing for fine-tuning of the ZnO structures optical properties and their application in photonics.

Materials and Methods

Typically, equimolar aqueous solutions of zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine (HMTA – $C_6H_{12}N_4$) are used for the ZnO nanostructures hydrothermal synthesis [6, 7]. Here, $Zn(NO_3)_2$ serves as a source of Zn^{2+} ions, and HMTA is a slowly decomposing base that provides an alkaline environment in solution and the desired amount of OH^- ions. Reactions occurring during the synthesis:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH^{4+} + OH^- \quad (2)$$

$$Zn(NO_3)_2 \leftrightarrow Zn^{2+} + 2NO_3 \quad (3)$$

$$2OH^- + Zn^{2+} \leftrightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad (5)$$

In this work, we employ conventional synthesis protocol using equimolar concentration $Zn(NO_3)_2$ and HMTA aqueous solutions. Synthesis is carried out on Si(111) substrates, which were preliminarily purified in acetone and then in isopropanol. Five samples were synthesized: Sample 1 – without the use of surfactants, Sample 2 – with sodium citrate and Sample 3 – with PEI. For ZnO surface nucleation we spin-coated the substrates with 3 seed layers of zinc acetate aqueous solution at a concentration of 5 mmol·L^{-1} [13].

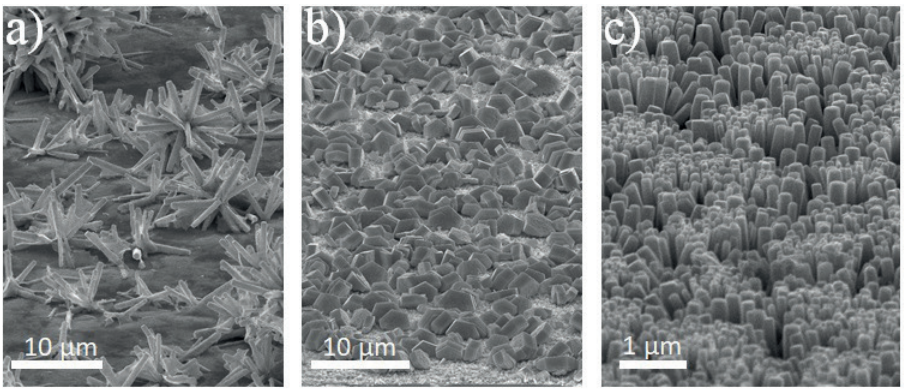

Fig. 1. Scanning electron microscopy (SEM) images of Sample 1 (branched NWs) (*a*); Sample 2 (hexapods) (*b*); Sample 3 (vertical NWs) (*c*)

For the growth, HMTA aqueous solution (with the surfactants for Samples 2 and 3) was added to the zinc nitrate solution in 200 ml Teflon cup with constant stirring. Sample 1 was grown with equimolar concentration of precursors of 300 mmol·L^{-1}. Samples with surfactants (2, 3) were grown with equimolar concentration of precursors of 100 mmol·L^{-1}. During the synthesis, a constant temperature of 85 °C was maintained. The synthesis duration for all samples was 3 hours.

The resulting structures are found to possess branched NWs shape with an aspect ratio (length to thickness ratio) of about 10:1 (Fig. 1, *a*), quasi-two-dimensional nanostructures [8] in the shape of hexapods with D ~ 5 µm, l ~ 1 µm (Fig. 1, *b*) and NWs with D ~ 100 nm and l ~ 1 µm (Fig. 1, *c*). Typical images of the synthesized ZnO nanostructures were obtained using a JSM 7001F scanning electron microscope (JEOL, Akishima, Tokyo, Japan).

Results and Discussion

The PL spectra of the synthesized samples were studied using an MDR-204-2 monochromator (LOMO-Photonics). The samples were placed in a closed-cycle helium cryostat (Janis Research Company, USA). The PL was excited by a He-Cd laser (excitation wavelength λ = 325 nm, maximum radiation power $W = 50$ kW·cm^{-2}). The sample temperature was varied in the 5–300 K range. The laser radiation intensity was controlled by neutral light filters. During the work, PL spectra were obtained for all samples (Fig. 2).

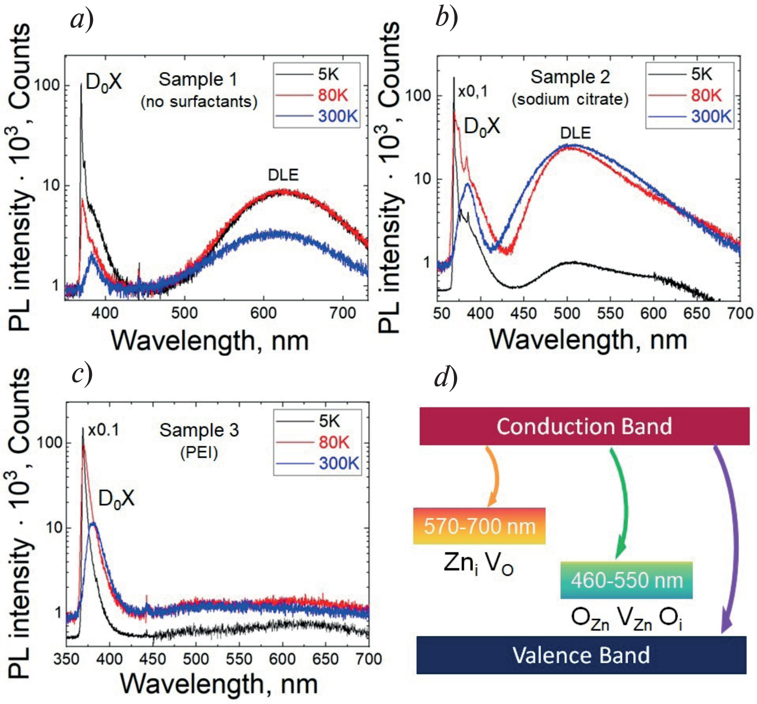

Fig. 2. PL spectra taken in a wide spectral range at different temperatures: (*a*) Sample 1 (without surfactant), (*b*) Sample 2 (with sodium citrate), NBE region of the spectrum is multiplied by 0.1, (*c*) Sample 3 (with PEI) NBE region of the spectrum multiplied by 0.1, (*d*) Schematic representation of the deep levels and corresponding radiative transitions

PL spectroscopy study demonstrates strong NBE emission in the UV region in all of the synthesized samples associated with an exciton on a neutral donor (D_0X). The obtained spectra demonstrate the different response in the visible range governed by the deep levels. The sample synthesized without the surfactants has an efficient response in the visible, centered near 620 nm. This band is often associated with excess zinc including Zn interstitial (Znin) and lack of oxygen such as vacancies (V_O) [6, 14, 15]. Use of sodium citrate leads to the DLE in the green region centered near 500 nm. This behavior is associated with the excess oxygen and zinc vacancies [6, 14, 15]. Use of PEI makes it possible to suppress the DLE. These effects are associated with a variation in the balance between zinc and oxygen ions in the growth solution provided by the change in the chemical composition of the growth medium.

Conclusion

The obtained results demonstrate the prospects for use of the technologically feasible hydrothermal method to develop light-emitting structures based on zinc oxide. The spectral characteristics of such structures can be tailored in a wide range by changing the growth medium composition opening the way for fabrication of UV-VIS and white light sources for biology, disinfection and lighting.

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REFERENCES

1. **Kondratev V.M., Morozov I.A., Vyacheslavova E.A., Kirilenko D.A., Kuznetsov A., Kadinskaya S.A., Nalimova S.S., Moshnikov V.A., Gudovskikh A.S., Bolshakov A.D.,** Silicon Nanowire-Based Room-Temperature Multi-environment Ammonia Detection, ACS Applied Nano Materials, 5 (7) (2022) 9940–9949.

2. **Kadinskaya S.A., Kondratev V.M., Kindyushov I.K., Kuznetsov A. and Punegova K.N.,** Hydrothermal ZnO-based Nanostructures: Geometry Control and Narrow Band UV Emission, 2022 Conference of Russian Young Researchers in Electrical and Electronic Engineering (ElConRus) 2022, 958–961.

3. **Kadinskaya S.A., Kondratev V.M., Kindyushov I.K., Labzovskaya M.E., Novikov B.V., Shtrom I.V., Lihachev A.I., Nashchekin A.V. and Bolshakov A.D.,** Hydrothermal zinc oxide nanostructures: geometry control and narrow band UV emission, J. Phys.: Conf. Ser. 2022, 2227, 012007.

4. **Kuznetsov A., Roy P., Kondratev V.M., Fedorov V.V., Kotlyar K.P., Reznik R.R., Vorobyev A.A., Mukhin I.S., Cirlin G.E., Bolshakov A.D.,** Anisotropic Radiation in Heterostructured "Emitter in a Cavity" Nanowire, Nanomaterials, 12 (2) (2022) 241.

5. **Look D.C., Claflin B., Alivov Y.I., Park S.J.,** The Future of ZnO Light Emitters. Phys. status solidi, 201 (2004) 2203–2212.

6. **Kadinskaya S.A., Kondratev V.M., Kindyushov I.K., Koval O.Yu., Yakubovsky D.I., Kusnetsov A., Lihachev A.I., Nashchekin A.V., Akopyan I.Kh., Serov A.Yu., Labzovskaya M.E., Mikushev S.V., Novikov B.V., Shtrom I.V., Bolshakov A.D.,** Deep-Level Emission Tailoring in ZnO Nanostructures Grown via Hydrothermal Synthesis. Nanomaterials, 13 (1) (2022) 58.

7. **Gerbreders V., Krasovska M., Sledevskis E., Gerbreders A., Mihailova I., Tamanis E., Ogurcovs A.,** Hydrothermal Synthesis of ZnO Nanostructures with Controllable Morphology Change. CrystEngComm 2020, 22.

8. **El-Shaer A., Mofor A.C., Bakin A., Kreye M., Waag A.,** High-Quality ZnO Layers Grown by MBE on Sapphire. Super-lattices Microstruct, 38 (2005) 265–271.

9. **Lee J., Choi Y., Kim J., Park M., Im S.,** Optimizing N-ZnO/p-Si Heterojunctions for Photodiode Applications. Thin Solid Films 2002, 403–404.

10. **Alivov Y.I., Johnstone D., Özgür U., Avrutin V., Fan Q., Akarca-Biyikli S.S., Morkoç H.,** Electrical and Optical Prop-erties of N-ZnO/p-SiC Heterojunctions. Jpn. J. Appl. Phys., 44 (2005) 7281–7284.

11. **Aziz T.N.T.A., Rosli A.B., Yusoff M.M., Herman S.H., Zulkifli Z.,** Transparent Hybrid ZnO-Graphene Film for High Stability Switching Behavior of Memristor Device. Mater. Sci. Semicond. Process, 89 (2019) 68–76.

12. **Zhou Z., Xiu F., Jiang T., Xu J., Chen J., Liu J., Huang W.,** Solution-Processable Zinc Oxide Nanorods and a Reduced Graphene Oxide Hybrid Nanostructure for Highly Flexible and Stable Memristor. J. Mater. Chem. C, 7 (2019) 10764–10768.

13. **Desai M.A., Sharma V., Prasad M., Jadkar S., Saratale G.D., Sartale S.D.,** Seed-Layer-Free Deposition of Well-Oriented ZnO Nanorods Thin Films by SILAR and Their Photoelectrochemical Studies. Int. J. Hydrogen Energy, 45 (2020) 5783–5792.

14. **Lima S.A., Sigoli F., Jafelicci Jr M., Davolos M.,** Luminescent Properties and Lattice Defects Correlation on Zinc Ox-ide. Int. J. Inorg. Mater., 3 (2001) 749–754.

15. **Lin B., Fu Z., Jia Y.,** Green Luminescent Center in Undoped Zinc Oxide Films Deposited on Silicon Substrates. Appl. Phys. Lett., 79 (2001) 943–945.

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